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REMOVAL OF SULFUR-CONTAINING COMPOUNDS FROM GAS AND OIL AND ANALYSIS OF DESULFURIZATION WASTE

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ABSTRACT

In its negative impact on the environment sulfur compounds take one of the leading places among the pollutants. Their negative consequences can be seen not only near the emission sources, but at a very considerable distance from them. Many facts point out the influence of anthropogenic emissions on the degree of contamination of the air by sulfur.

This work is devoted to methods of effective removal of oil and gas from the sulfur-containing compounds, the influence of various modified adsorbents on the cleaning performance, as well as certain qualitative composition of the resulting sulfur - desulfurization waste hydrocarbon raw materials for use in various industries.

KEYWORDS: Oil, Technology, Refining Methods, Desulfurization Waste, Adsorbent, Mercaptan, Hydrogen Sulfide, Sulfur

INTRODUCTION

The presence of aggressive sulfur compounds in the ground mass of hydrocarbons in the most fields of Western Kazakhstan create difficulties in production, transportation, storage and processing, which makes desulfurization of petroleum and petroleum products particularly relevant issue.

Free sulfur is formed during petroleum and sulfur-containing gases refining process as a result of oxidation by the conventional technology. Even with the partial realization, the stock of sulfur increases. Sulfur piles are a growing threat to the ecological security of the region.

The essential problem is the presence of hydrogen sulfide in the fields of Zhanajol and Tengiz as well. The lack of processing and sulfur application techniques leads to serious environmental problem. Sulfur clusters are mostly accumulated in the process of petroleum refining. With an annual capacity of 3 million tons of crude oil a stable daily produces about 1,000 tons of sulfur. The inevitable consequence is the technological impact of accumulated elemental sulfur and hydrogen sulfide on the environment.

In order to use clean, renewable energy sources for cleaning gas characteristics of helioirradiated aluminosilicate were investigated - metallurgical wastes.

Adsorption properties of aluminosilicate tested in the chemical laboratory of the Zhanazhol gas processing plant. The properties of the three samples of the adsorbent have been studied: 1 - control (untreated), 2 - helioirradiated, treated in

the conventional glass tube, 3 – helioirradiated, treated in a quartz tube (Table 1). Hydrogen sulfide and mercaptan in petroleum gas were estimated by the iodometric method, the essence of which is the absorption of hydrogen sulfide and mercaptans from gas with the help of acidified solution of $CdCl_2$ and subsequent iodometric titration formed CdS.

The pre-stack was the initial concentration of hydrogen sulfide gas with 31 g/m3.

Carrying out the Experiment

A sample of the gas tested was displaced from the pipette by 10 to 15--fold volume displacing gas through the adsorbing flask. At the beginning of the scavenging, gas velocity 1-2 bubbles per second was set. When the main portion of the gas has been expelled into the solution, the speed was gradually increased to 20 dm^3 / h.

After finishing that process, the content of the absorption bottles were analyzed. The contents of the first flask were transferred quantitatively into conical flask for titration, rinsed thoroughly the tube wall of the flask with distilled water and poured it into the same flask.

10 cm^3 iodine solution recommended concentration was added with a pipette into the flask and making its excess by brown color of the solution, the excess of iodine was titrated with sodium thiosulfate $Na_2S_2O_3$ concentration corresponding to a light yellow color. Then 1 cm^3 of starch solution was added and continue to titrate to the disappearance of the blue color.

Contents of the second absorption bottle was analyzed as the content of the first one.

Simultaneously to the analysis of the tested gas sample, control experiment was performed in the same manner as described above but without the transmission of gas.

Processing of results

Concentration of hydrogen sulfide in the gas X, g/m^3, calculated by the formula

$$X = (V-V_1)\ C\ 17 / V_2\ K,\ g/m^3 \tag{1}$$

V- Volume of titrant $Na_2S_2O_3$, consumed for the titration of the absorption solution without passing gas (control), cm^3;

V_1- Volume of titrant $Na_2S_2O_3$, consumed for the titration of the absorption solution after passing the test gas, cm^3;

V_2 - Volume of gas measured by the gas meter, dm^3;

C - Concentration of titrant $Na_2S_2O_3$, mol / dm ^{3};

K - Coefficient of reduction of gas volume to standard conditions - a temperature of 20 ^{0}C and pressure 101, 325 kPa;

17 - The mass of hydrogen sulfide, corresponding to 1 cm^3 $Na_2S_2O_3$ titrant concentration of exactly 1 mol / dm ^{3} mg.

0.5 dm^3 gas was transferred. After passing the gas through the flask with sorbents №2 and 3 absorption of moisture in the gas was observed.

As shown in Table 1, after passing the gas through a flask with an adsorbent №3 hydrogen sulphide content was lower, indicating the positive effects of solar radiation exposure of the adsorbent. Thus, the use of helioirradiation in the usual glass to activate aluminosilicate made it possible to reduce the concentration of hydrogen sulfide in oil gas by 23 times, and in quartz glass up to 456 times. The absorptive capacity and adsorption capacity of the carbon adsorbent based on rice husk for cleaning oil and gas from the sulfur-containing compounds were studied next.

Table 1: Hydrogen Sulfide in Gas While Passing it Through Aluminosilicate

Sample of Aluminosilicate	No Absorption Bottles	Concentration H_2S, G/M3
№1 - untreated	1	16,4
	2	3,2
	3	2,5
№2 treated in the usual glass	1	15,83
	2	2,2
	3	1,36
№3 treated in quartz	1	13,2
	2	0,17
	3	0,068

Tests were carried out in the chemical analytical laboratory of the Zhanazhol gas processing plant. Concentration of hydrogen sulfide and mercaptans in the gas was determined by the international standard ISO 6326-4. The initial concentration of hydrogen sulfide gas with 58.89 g/m3, 447 g/m3 mercaptan (Table 2).

Carrying out of the Experiment

2 g adsorbent was placed in a column the lower part of which by the help of the rubber tube was attached to a gas meter drum (GSB- type 400 cells, P 5885 Pa) for controlling the volume and rate of passage of gas to be purified. On the other side the counter was connected with a gas sampler. The upper part of the column, through which the purified gas comes out, was attached to the chromatograph. Gas was passed through the bottom of the column at about 1 liter / min. Using carbon adsorbent made it possible to purify16 liters of gas and significantly reduce the mercaptan content in it (almost 5 times). Hydrogen sulphide is a very undesirable component of sulphurous oils, exemption from which requires a significant consumption of reagents, construction of special facilities, etc. It may be present in the associated gas accompanying sulfur oil dissolved in the oils themselves, in the primary oil distillation products (gases, gasoline distillates and other light oil) or in the products of secondary thermal process (thermal and catalytic cracking, catalytic reforming, hydrofining and etc.). The content of hydrogen sulfide and mercaptans in oil was determined by gas chromatography according to GOST (All Union State standard) P 50802-95. As the initial was taken density of the oil 0, 8027 g/cm^3 (Table 3).

Table 2: Gas Purification from Hydrogen Sulfide and Mercaptan with the Help of Carbon Adsorbent

The Volume of Transmitted Gas	Concentration H_2S, G/M^3	Concentration of RSH, G/M3
Source gas	58,89	447
2 L	trans.	87
4 L	«	87
8 L	«	86
10 L	«	86
12 L	«	86
16 L	«	87
20 L	6,44	125

Carrying out the Experiment

500 ml oil at 60 drops / min was passed through the adsorbent layer with the mass of 5 g.

Usage of carbon adsorbent reduced the concentration of the lower mercaptans in oil by 3-10 times and thoroughly cleaned from hydrogen sulfide.

Table 3: Oil Cleaning Results Using Carbon Adsorbent

No Sample	Content mg / l					
	Before Treatment			After Treatment		
	Hydrogen Sulfide	Methyl Mercaptan	Ethyl Mercaptan	Hydrogen Sulfide	Methyl Mercaptan	Ethyl Mercaptan
1	46,62	55,57	283	Отс.	4,92	76,7
2	44,03	50,33	252	Отс.	4,68	65,6
3	45,89	54,45	281	Отс.	4,76	69,8

From the results of analysis we can see that carbon adsorbent can absorb hydrogen sulfide and mercaptans from oil and gas. Studies using a modified carbon adsorbent for purifying gasoline mercaptans was also carried out. Inoculation of adsorbent was carried out with 10 % solutions of magnesium salts ($MgCl_2$), and copper ($CuCl_2$).

Carrying out the Experiment

Purification of gasoline from mercaptan sulfur was carried out in dynamic conditions. 1 g of test adsorbent was placed in a glass column with a diameter of 10 mm and the gasoline with flow rate at 0.5 ml / min. Samples were collected at 25 ml. In the analyzed fractions, the residual mercaptan sulfur content by potentiometric titration with silver ammine was determined.

- Source adsorbent (carbon). Passed through the adsorbent 500 ml of gasoline containing mercaptan sulfur content of 0.0004 %. Absorbed 0.32 mg / g (0.01 meq / g) (Table 4).

Table 4: Results of Cleaning Gasoline from Mercaptans with Source of Carbon Adsorbents

No Fraction	Remaining Mercaptan Sulfur, Mg	Absorption, Mg / G	Absorption, %
1-14	0,056	0,019	25,34
15	0,075	0	0

- Adsorbent, modified $CuCl_2$. Conceded 500 ml gasoline containing mercaptan sulfur 0.0003%. Trapped 0.236 mg / g (0.007 mEq / g) (Table 5).

Table 5: Results of Cleaning Gasoline from Mercaptans with Carbon Adsorben, T Modified $Cucl_2$

No. Fraction	Remaining Mercaptan Sulfur Mg	Absorption, Mg	Absorption, %
1-7	0,0375	0,0185	33
8-15	0,045	0,011	19,6
16	0,056	0	0

- Adsorbent, modified $MgCl_2$. Conceded 350 ml gasoline containing mercaptan sulfur 0.0006 %. Absorbed 1.14 mg / g (0.034 meq / g) (Table 6).

Table 6: Results of Cleaning Gasoline from Mercaptans with Carbon Adsorben, Modified $Mgcl_2$

No Fraction	Remaining Mercaptan Sulfur Mg,	Absorption Mg / G	Absorption, %
1	0,0375	0,075	67
2-6	0,056	0,056	50

Table 6: Contd.,

7-11	0,075	0,0375	33
12-18	0,093	0,0188	16,7
19	0,099	0	0

As seen from Table 6, treatment is effective for the first fraction.

Table 7: Purification of Gasoline from Mercaptans with Carbon Adsorbent

Sample of Adsorbent	Amount of Missed Gasoline, ml	Original Content of Mercaptans in Gasoline, %	Absorption Efficiency, mg / g (meq / g)	Efficiency Absorption (max), %
Initial	500	0,0004	0,32 (0,01)	25,3
$CuCl_2$ Modified	500	0,0003	0,236 (0,007)	33
$MgCl_2$ Modified	350	0,0006	1,14 (0,034)	67

Experimental data suggest that the greatest absorption is observed for adsorbent modified $MgCl_2$, - up to 67 %.

Tengiz (Atyrau) and Zhanazhol (Aktobe) oil and gas fields are characterized by a very high content of sulfur compounds. Recoverable amounts of hydrocarbons are millions of tons per year [1]. It is planned to increase crude oil output and, consequently, resources of sulfur will increase as well. Even with the partial implementation, sulfur reserves continue to grow.

For elemental sulfur MPC = 6.0 mg/m^3, aerosol, hazard class 4. Threshold concentration of sulfur in the air of settlements is not more than 0.010 mg/m^2 (by inhalation for no more than 1 hour). Maximum permissible emission of sulfur is recommended no more than 10 tons per year [2].

To determine the quality of the sulfur produced during desulfurization of oil and gas, as well as a comparative analysis of average samples were taken sulfur - oil and gas waste of Zhanazhol and Tengiz fields.

Carrying out the Experiment

Samples were processed by means of quartering. Chemical analysis was carried out according to the specified Standard [3]. Scaly and granulated sulfur from Tengiz field were taken as samples for determination of arsenic and selenium. Arsenic in sulphur was analyzed by the method of "sample Marche." This method makes it possible to detect arsenic to 1×10^{-6} g in various objects. Weighed sulfur sample (50 g) was ground in a porcelain mortar, 10 g zinc dust and 150 ml of 2^n hydrochloric acid were added were to it, then the mixture was placed in a flask of 0.5 liters, then it was sealed with a rubber stopper with glass tube. Arsine gas (AsH_3) in admixture with hydrogen is formed in the reaction mixture, in the presence of arsenic compounds. The mixture of these gases were ignited and a glazed porcelain cold plate was brought to the oxidation part of the flame. On its surface, we can find arsenic in the form of raid (mirror) of steel-gray color. Such plaque is also formed in the presence of antimony compounds (interferences). However [4], arsenic mirror can be distinguished from antimony with 10 % solution of ammonium polysulphide. This solution dissolves plaque antimony, arsenic plaque remains unchanged.

These experiments showed a negative reaction for arsenic in samples from the Tengiz sulfur. Selenium content of sulfur was determined by the same Standard. The remaining impurities are regulated by the mentioned above Standard. The results of the research on the quality of the Zhanazhol and Tengiz sulfur are shown in Table 8. Table 8 shows that in comparison to samples from the Zhanazhol lump sulfur, which has high content of impurities, the samples of sulfur from

the Tengiz field meet the requirements of the Standard in all items of ingredients. In the analysis of the mass fraction of moisture, the method based on the gravimetric determination of mass loss by drying at a temperature of 70±2^{0}C was used. The mass fraction of organic substance was found by the method based on the gravimetric determination of the residue on the mass difference between the double sample calcination at 250±10^{0}C and 800±10^{0}C. Mass fraction of acid in sulfur has been restated to sulfuric acid. The method is based on the extraction of the acidic substance with water and titrating the obtained extract with sodium hydroxide in the presence of phenolphthalein indicator. The weight proportion of ash is determined by calcination of a sample at a temperature of 800±10^{0}C and weighing the remnants.

Mass fraction of sulfur is determined based on dry substance.

Table 8: Comparison of the Quality of Sulfur from the Tengiz and Zhanazhol Fields with the Standard, Grade 9998-9920 (Mass Fractions are given in %)

Names Density	Grade 9998	Grade 9995	Grade 9990	Grade 9950	Grade 9920	Sulfur Granular Tengiz	Sulfur «scaly» Tengiz	Sulfur Zhanazhol
1. Mass fraction of sulphur	99,2800	99,2500	99,9000	99,5000	99,200	99,9800	99,9800	99,06
2. Mass fraction of ash	0,02000	0,03000	0,05000	0,02000	0,04000	0,00990	0,01000	0,390
3. Mass fraction of organic substance	0,01000	0,03000	0,0600	0,02500	0,05000	0,00590	0,00780	0,53
4. Mass fraction of acid (по H_2SO_4)	0,0015	0,0030	0,0040	0,0100	0,0200	0,00023	0,000023	0,02
5. Mass fraction of moisture	0,200	0,200	0,200	0,200	0,00020	0,00023	0,00023	0,8
6. Mass fraction of arsenic	0,0000*	0,0000*	0,0000*	0,0000*	0,0300	Less than 10^{-6}	Less than 10^{-6}	Less than 10^{-6}
7. Mass fraction of selenium	0,0000*	0,0000*	0,0000*	0,0000*	0,0400	traces	traces	traces
8. Mechanical impurities	Absence	absence	absence	absence	absence	not found	not found	–
* - not found								

Difference in structure and composition of sulfur samples confirmed with the results of the IR spectroscopic study of the structure of technical sulfur from the Tengiz and Zhanazhol fields compared to net pharmacy sulfur shown in Table 9.

Table 9: Spectral Composition of the Absorption Bands of Granulated Sulfur Samples (№ 1) from Tengiz and Sulfur Powder (№ 2) from Zhanazhol

Frequency, cm^{-1}	Frequency, cm^{-1}
Sample №1	Sample №2
600*	940
657	1120*
800	1220
854	1268
920	1313
960	1650*
1020	
1050	
1068	
1227	
1281	
1650*	

Composition of the Zhanazhol sulfur, unlike sulfur from the Tengiz field, is characterized by a high content of organic components, most of which are n- alkanes with an admixture of cyclic hydrocarbons.

Radioactivity of the granulated sulfur from Tengiz defined in LLP "Zap KazEco service" on the device Bella-1 and a scaling apparatus for measuring radioactivity sensor type STS -100 measuring gamma radioactivity was not different from the background.

Thus, lump sulfur from the Zhanazhol field with decreasing of the mass fraction of some impurities and enforcement of indicators in accordance with the Standard, may be suitable for industrial use. Granulated and scaly sulfur obtained while purification of oil and gas from Tengiz, meets all the requirements of the Standard, can be used as raw materials in various industries.

RESULTS

Thus, the carbon adsorbent effectively absorbs from hydrocarbon gas such corrosive sulfur compounds as hydrogen sulfide and mercaptans . The efficiency of the proposed carbon adsorbent with desulphurization of oil, which has allowed to reduce the concentration of the lower mercaptans by 3-10 times and thoroughly removal of hydrogen sulfide. At the same time revealed that composition of the Zhanazhol sulfur, unlike sulfur from the Tengiz field, is characterized by a high content of organic components most of which are n- alkanes with an admixture of cyclic hydrocarbons.

CONCLUSIONS

The experiments developed new methods of active adsorbents for purification of petroleum hydrocarbons from sulfur compounds, carbon adsorbent efficiency has been defined in desulfurization of crude oil and natural gas, as well as the qualitative composition of sulfur was studied, obtained in the purification of oil and gas deposits in Tengiz and Zhanazhol to further use in various industries.

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